

1 alumino-silicate catalyst to form higher molecular weight hydrocarbons and hydrobromic
acid (coupling), (3) neutralizing the hydrobromic acid by reaction with an aqueous solution of
partially oxidized metal bromide salts (as metal oxides/oxybromides/bromides) to produce a
metal bromide salt and water in an aqueous solution, or by reaction of the hydrobromic acid
5 with air over a metal bromide catalyst, and (4) regenerating bromine by reaction of the metal
bromide salt with oxygen to yield bromine and an oxidized salt. Potential drawbacks of the
processes include low methane conversions; short space-times and the resulting potential for
less than 100% bromine conversion; wasteful overbromination of ethane, propane, and higher
alkanes, resulting in the formation of dibromomethane and other polybrominated alkanes,
10 which will likely form coke under the disclosed reaction conditions; comparatively low alkyl
bromide conversions; the need to separate the hydrocarbon product stream from an aqueous
hydrohalic acid stream; and inadequate capture of halogen during the regeneration of the
catalyst to remove halogen-containing coke. In addition, the proposed venting of this
bromine-containing stream is both economically and environmentally unacceptable.

15 [0006] The Waycuilis process also apparently requires operation at relatively low
temperatures to prevent significant selectivity to methane. The likely result would be
incomplete conversion of alkyl bromide species and, because the described process relies on
stream splitting to recover products, a considerable amount of unconverted alkyl bromides
20 would likely leave the process with the products. This represents an unacceptable loss of
bromine (as unconverted methyl bromide) and a reduced carbon efficiency.

25 [0007] The neutralization of hydrobromic acid by reaction with an aqueous solution of
partially oxidized metal bromide salts and subsequent reaction of the metal bromide salts
formed with oxygen to yield bromine and an oxidized salt, as disclosed by Waycuilis, also
has a number of disadvantages. First, any carbon dioxide present will form carbonates in the
slurry, which will not be regenerable. Second, the maximum temperature is limited due to
pressure increases which are intolerable above approximately 200 °C, thus preventing
complete recovery of halogen. Third, although the use of redox-active metal oxides (e.g.,
30 oxides of V, Cr, Mn, Fe, Co, Ce, and Cu) will contribute to molecular bromine formation
during the neutralization of hydrobromic acid, incomplete HBr conversion due to the use of a
solid bromide salt will in turn result in a significant loss of bromine from the system (in the
water phase). Provided an excess of air was used, the bromide salt might eventually be
converted to the oxide form, stopping any further loss of HBr in the water discard.

35 [0008] To separate water from bromine, Waycuilis discloses the use of condensation and
phase separation to produce semi-dry liquid bromine and a water/bromine mixture. Other
means for separating water from bromine, such as using an inert gas to strip the bromine from
the water phase or using adsorption-based methods have also been proposed by others;

however, such methods are minimally effective and result in a significant overall loss of halogen.

[0009] The prior art oxychlorination process first removes the water from HCl (a costly step) and then reacts the HCl with oxygen and hydrocarbon directly. Oxychlorination processes rely on the separation of HCl from the unreacted alkanes and higher hydrocarbon products by using water absorption, and subsequent recovery of anhydrous HCl from the aqueous hydrochloric acid. U.S. Pat. No. 2,220,570 discloses a process and apparatus for the absorption of HCl in water where the heat of absorption is dissipated by contacting the HCl gas with ambient air, and also by the vaporization of water. A process for producing aqueous hydrochloric acid with a concentration of at least 35.5 wt% by absorbing gaseous HCl in water is disclosed in U.S. Pat. No. 4,488,884. U.S. Pat. No. 3,779,870 teaches a process for the recovery of anhydrous HCl gas by extractive distillation using a chloride salt. U.S. Pat. No. 4,259,309 teaches a method for producing gaseous HCl from dilute aqueous HCl using an amine together with an inert water-immiscible solvent.

[0010] Although researchers have made some progress in the search for more efficient CH bond activation pathways for converting natural gas and other hydrocarbon feedstocks into fuels and other products, there remains a tremendous need for a continuous, economically viable, and more efficient process.

SUMMARY

[0011] In one embodiment of the present disclosure, a continuous process for converting methane, natural gas, and other hydrocarbon feedstocks into one or more higher hydrocarbons or olefins is provided. In one embodiment of the present disclosure, the process includes the steps of alkane halogenation, "reproportionation" of polyhalogenated compounds to increase the amount of monohalides that are formed, oligomerization (C-C coupling) of alkyl halides (and optionally, olefins) to form higher carbon number products, separation of products from hydrogen halide, continuous regeneration of halogen, and separation and recovery of molecular halogen from water.

[0012] The present disclosure exploits the discovery that, following consumption of substantially all of the molecular halogen in an alkane halogenation reactor, polyhalogenated hydrocarbons that are formed can be reacted with unhalogenated alkanes to improve the overall yield of monohalides, which react in later process steps more efficiently -- and form more desirable products -- than polyhalogenated species. After the initial alkane halogenation reaction, which consumes substantially all of the molecular halogen, additional halogenation is accomplished by transfer of halogen from polyhalogenated alkanes to unhalogenated alkanes, thereby reducing carbon loss and coke formation. For example, dibromomethane can be

reproportionated with methane to form methyl bromide, and dibromomethane can be reproportionated with ethane or propane to form ethyl bromide and ethylene and/or propyl bromide and propylene. Although not bound by theory, it is believed that, in some embodiments, monohalide enrichment also proceeds via olefin formation followed by
5 reaction with polyhalogenated alkanes. In some embodiments, reproportionation is facilitated by a catalyst.

[0013] The present disclosure provides a number of unique subprocesses, improvements, and advantages, including reproportionation of polyhalides; recovery of halogen released during the requisite coke burn off; continuous regeneration of molecular halogen through the
10 reaction of hydrogen halide and oxygen over a catalyst (allowing the overall process to operate continuously); and use of carefully selected anti-corrosion materials to address the inherently corrosive nature of the halogen-based process (allowing the process to be practiced commercially); and use of appropriate, reliable catalysts for long-term halogen generation. The bromination reactor can be operated adiabatically and over a wide temperature range.
15 Carbon dioxide and water are easily tolerated, as are trace hydrocarbon impurities. Carbon loss due to coke formation is minimized by design by preferentially reacting monohalides over a coupling catalyst such as a zeolite or other reactive metal-oxygen material. Complete recovery of halogen for reuse is also an important advantage of the present disclosure.

[0013a] In an aspect, there is provided a method comprising: providing a halogen stream;
20 providing a first alkane stream; reacting at least a portion of the halogen stream with at least a portion of the first alkane stream to form a halogenated stream, wherein the halogenated stream comprises alkyl monohalides, alkyl polyhalides, and a hydrogen halide; providing a second alkane stream; reacting at least a portion of the second alkane stream with at least a portion of the alkyl polyhalides to create at least some additional alkyl monohalides; and
25 contacting at least some of the alkyl monohalides and at least some of the additional alkyl monohalides with a catalyst to form a product stream that comprises higher hydrocarbons and hydrogen halide.

[0013b] In another aspect, there is provided a system for forming hydrocarbons comprising: a halogenation reactor, wherein the halogenation reactor receives a quantity of
30 halide and a first quantity of alkane and produces a halogenated product, the halogenated product comprising an alkyl monohalide product and an alkyl polyhalide product; a reproportionation reactor, wherein the reproportionation reactor receives the halogenated product and a second quantity of alkane and produces at least some additional alkyl

monohalide product and a quantity of hydrogen halide; and an oligomerization reactor comprising a catalyst, wherein the oligomerization reactor receives the alkyl monohalide product and the additional alkyl monohalide product and produces a quantity of hydrocarbon product and a second quantity of hydrogen halide.

5 [0013c] In yet another aspect, there is provided a method comprising: providing an alkyl halide stream comprising alkyl monohalides, alkyl polyhalides, and a hydrogen halide; providing a first alkane stream; reacting at least a portion of the first alkane stream with at least a portion of the alkyl halide stream to create at least some additional alkyl monohalides; contacting at least some of the alkyl monohalides and at least some of the additional alkyl
10 monohalides with a catalyst to form a product stream that comprises higher hydrocarbons, hydrogen halide, and any unreacted portion of the first alkane stream; separating the unreacted portion of the first alkane stream from the product stream; providing a halogen stream; and reacting at least some of the unreacted portion of the first alkane stream separated from the product stream with the halogen to form the alkyl halide stream.

15 [0014] These discoveries, integrated into an overall process, are the basis for the invention and offer a true advance for such applications as the conversion of natural gas to liquid fuels (including gasoline and gasoline additives) and chemicals (including aromatics, such as benzene, xylene, and toluene, and light olefins, such as ethylene and propylene).

BRIEF DESCRIPTION OF THE DRAWINGS

20 [0015] FIG. 1 is a schematic view of one embodiment of a continuous process for converting methane or natural gas into hydrocarbon chemicals according to the invention;

[0016] FIG. 2 is a schematic view of one embodiment of a continuous process for converting methane or natural gas into hydrocarbon fuels according to the invention;

25 [0017] FIG. 3 is a schematic view of a subprocess for reportionating polyhalides according to an alternate embodiment of the invention;

[0018] FIG. 4 is a schematic view of one embodiment of a monobromide separation column, for use in the practice of the invention;

[0019] FIG. 5 is a schematic view of one embodiment of an extractive distillation system, for use in the practice of the invention

1 [0020] FIG. 6 is a simplified block diagram of one embodiment of a continuous process for converting alkanes into hydrocarbon products according to the invention, wherein water is separated from hydrocarbon products;

5 [0021] FIG. 7 is a simplified block diagram of one embodiment of a continuous process for converting alkanes into hydrocarbon products according to the invention, wherein water is separated after the alkane bromination step;

[0022] FIG. 8 is a graph of bromobenzene conversion and benzene yield as a function of
10 time, for an experiment conducted according to one embodiment of the invention; and

[0023] FIG. 9 is a graph of catalyst effectiveness as a function of time, for an experiment conducted according to one embodiment of the invention.

15 DETAILED DESCRIPTION

[0024] The present invention provides a chemical process that enables natural gas and other hydrocarbon feedstocks to be converted into higher molecular weight hydrocarbon products, using molecular halogen to activate C-H bonds in the feedstock. According to one
20 aspect of the invention, a continuous process for converting a hydrocarbon feedstock into one or more higher hydrocarbons comprises the steps of (a) forming alkyl halides by reacting molecular halogen with a hydrocarbon feedstock (preferably a feedstock containing methane), under process conditions sufficient to form alkyl halides and hydrogen halide, whereby substantially all of the molecular halogen is consumed; (b) forming reproporionated
25 alkyl halides by reacting some or all of the alkyl halides with an alkane feed, whereby the fraction of monohalogenated hydrocarbons present is increased; (c) contacting the reproporionated alkyl halides with a first catalyst under process conditions sufficient to form higher hydrocarbons and additional hydrogen halide; (d) separating the higher hydrocarbons from the hydrogen halide; (e) regenerating molecular halogen by contacting the hydrogen
30 halide with a second catalyst in the presence of a source of oxygen, under process conditions sufficient to form molecular halogen and water; (f) separating the molecular halogen from water to allow reuse of the halogen; and (g) repeating steps (a) through (f) a desired number of times. These steps can be carried out in the order presented or, alternatively, in a different order.

35 [0025] According to a second aspect of the invention, a continuous process for converting a hydrocarbon feedstock into one or more higher hydrocarbons comprises the steps of (a) forming alkyl halides by reacting molecular halogen with a hydrocarbon feedstock containing

1 methane in a halogenation reactor, under process conditions sufficient to form alkyl halides
and hydrogen halide, whereby substantially all of the molecular halogen is consumed; (b)
separating unreacted methane from the alkyl halides and directing it back into the
halogenation reactor; (c) forming repropportionated alkyl halides by reacting some or all of the
5 alkyl halides with an alkane feed containing at least 1% by volume of one or more C2-C5
hydrocarbons, whereby the fraction of monohalogenated hydrocarbons present is increased;
(d) contacting the repropportionated alkyl halides with a first catalyst under process conditions
sufficient to form higher hydrocarbons and additional hydrogen halide; (e) separating the
higher hydrocarbons from the hydrogen halide; (f) regenerating molecular halogen by
10 contacting the hydrogen halide with a second catalyst in the presence of a source of oxygen,
under process conditions sufficient to form molecular halogen and water; (g) separating the
molecular halogen from water to allow reuse of the halogen; and (h) repeating steps (a)
through (g) a desired number of times.

15 [0026] In each of the aspects and embodiments of the invention, it is intended that the
alkyl halides formed in step (a) can be all the same (e.g., 100% bromomethane) or, more
typically, different (e.g., mixtures of bromomethane, dibromomethane, dibromoethane, etc).
Similarly, it is contemplated that the "higher hydrocarbons" formed in step (c) can be all the
same (e.g., 100% isooctane) or, more typically, different (e.g., mixtures of aliphatic and/or
20 aromatic compounds). As used herein, the term "higher hydrocarbons" refers to
hydrocarbons having a greater number of carbon atoms than one or more components of the
hydrocarbon feedstock, as well as olefinic hydrocarbons having the same or a greater number
of carbon atoms as one or more components of the hydrocarbon feedstock. For instance, if
the feedstock is natural gas --typically a mixture of light hydrocarbons, predominately
25 methane, with lesser amounts of ethane, propane, and butane, and even smaller amounts of
longer chain hydrocarbons such as pentane, hexane, etc. -- the "higher hydrocarbon(s)"
produced according to the invention can include a C₂ or higher hydrocarbon, such as ethane,
propane, butane, C₅+ hydrocarbons, aromatic hydrocarbons, etc., and optionally ethylene,
propylene, and/or longer olefins. The term "light hydrocarbons" (sometimes abbreviated
30 "LHCs") refers to C₁-C₄ hydrocarbons, e.g., methane, ethane, propane, ethylene, propylene,
butanes, and butenes, all of which are normally gases at room temperature and atmospheric
pressure.

[0027] Nonlimiting examples of hydrocarbon feedstocks appropriate for use in the
present invention include alkanes, e.g., methane, ethane, propane, and even larger alkanes;
35 olefins; natural gas and other mixtures of hydrocarbons. In most cases, the feedstock will be
primarily aliphatic in nature. Certain oil refinery processes yield light hydrocarbon streams
(so-called "light-ends," typically a mixture of C₁ - C₃ hydrocarbons), which can be used with
or without added methane as the hydrocarbon feedstock in one embodiment of the invention.

1 [0028] Representative halogens include bromine (Br_2) and chlorine (Cl_2). It is also
contemplated that fluorine and iodine can be used, though not necessarily with equivalent
results. Some of the problems associated with fluorine can likely be addressed by using
dilute streams of fluorine (e.g., fluorine gas carried by helium, nitrogen, or other diluent). It
5 is expected, however, that more vigorous reaction conditions will be required for alkyl
fluorides to couple and form higher hydrocarbons, due to the strength of the fluorine-carbon
bond. Similarly, problems associated with iodine (such as the endothermic nature of certain
iodine reactions) can likely be addressed by carrying out the halogenation and/or coupling
reactions at higher temperatures and/or pressures. The use of bromine or chlorine is
10 preferred, with bromine being most preferred.

[0029] FIGS. 1 and 2 schematically illustrate two nonlimiting embodiments of a process
according to the invention, with FIG. 1 depicting a process for making hydrocarbon
chemicals (e.g., benzene, toluene, xylenes, other aromatic compounds, etc.), and FIG. 2
15 depicting a process for making fuel-grade hydrocarbons, e.g., hydrocarbons comprising a
predominant amount of C_5 and higher aliphatic hydrocarbons and (optionally) aromatic
hydrocarbons. The primary difference in the two embodiments is that the process depicted in
FIG. 2 lacks the first separation unit (SEP I) and does not return polybrominated species to
the bromination reactor for "reproportionation." In the scheme shown in FIG. 2, the amount
20 of polybromides produced is reduced significantly by introducing light gasses into the
bromination reactor. The polybromides (from methane bromination) react with the light
gasses to form monobromoalkanes. For convenience, the figures depict a bromine-based
process. In alternate embodiments of the invention, however, chlorine or other halogens are
used.

25 [0030] As shown in FIG. 1, natural gas (or another hydrocarbon feedstock) and molecular
bromine are carried by separate lines 1, 2 into a heated bromination reactor 3 and allowed to
react. Products (HBr , alkyl bromides, optionally olefins), and possibly unreacted
hydrocarbons, exit the reactor and are carried by a line 4 into a first separation unit 5 (SEP I),
30 where monobrominated hydrocarbons and HBr are separated from polybrominated
hydrocarbons. The polybromides are carried by a line 6 back to the bromination reactor,
where they undergo "reproportionation" with methane and/or other light hydrocarbons, which
are present in the natural gas and/or introduced to the bromination reactor as described below.

[0031] Reproportionation of the polybromides formed during the bromination reaction
35 enriches the outlet stream with monobromides and olefinic species, and reduces the amount
of polybrominated hydrocarbons that enter the coupling reactor. This, in turn, reduces the
amount of coke that forms during the carbon-carbon coupling reactions. For large scale
production of aromatic hydrocarbons, it is possible to employ additional separation units,

1 which can further purify the feed stream to the coupling reactor by separating and recycling
the polybromides, thereby reducing the amount of coke and the overall bromine requirement.

5 [0032] Unreacted hydrocarbon feedstock, HBr, monobromides, and (optionally) olefins
formed in the bromination reactor are carried by a line 7, through a heat exchanger 8, and
enter a heated coupling reactor 9, where the monobromides (and, optionally, any olefins
present) react in the presence of a coupling catalyst to form higher hydrocarbons. HBr,
higher hydrocarbons, and (possibly) unreacted hydrocarbons and alkyl bromides exit the
coupling reactor and are carried by a line 10, through another heat exchanger 11, and enter an
10 HBr absorption unit 12. Water is introduced into the unit through a separate line 13. HBr is
absorbed in this unit, which may be a packed column or other gas-liquid contacting device.
The effluent, containing liquid hydrocarbons and aqueous HBr, is carried by a line 14 to a
liquid-liquid splitter 15, which phase-separates liquid hydrocarbons from the aqueous HBr
stream. The liquid hydrocarbon products are then carried by a line 16 to a product clean-up
15 unit 17 to yield final hydrocarbon products.

20 [0033] After HBr is separated from the hydrocarbon products and unreacted methane
(and any other light hydrocarbons that may be present) in the HBr absorption unit, the
methane (and other light hydrocarbons, if any) is carried by a line 18 into a second separation
unit 19 (SEP II), which employs pressure- or temperature-swing adsorption, membrane-based
separation, cryogenic distillation (preferable for large scale production), or another suitable
separation technology. Methane, and possibly other light hydrocarbons, are returned to the
bromination reactor via one or more lines 20, 21. In the embodiment shown, methane is
directed to an upstream region or "zone" of the bromination reactor, while other light
hydrocarbons are directed to a mid- or downstream zone of the reactor (the latter to facilitate
25 reportionation of polybromides).

30 [0034] The aqueous HBr stream that evolves from the liquid-liquid splitter is carried by a
line 22 to a bromine generation unit 23. Oxygen, air, or oxygen-enriched gas is also fed into
the unit through a separate line 24. Bromine is regenerated by reacting HBr with oxygen in
the presence of a suitable catalyst. The resulting stream contains water, molecular bromine,
oxygen, nitrogen (if air was used as the source of oxygen), and possibly other gases. This
product stream is carried by a line 25 through a heat exchanger 26 into a flash vaporization
unit 27, which separates most of the molecular bromine from water, oxygen, nitrogen, and
other gases (if any) that are present. Molecular bromine, either as a liquid or vapor (and
35 containing no more than a trace of H₂O), is carried by a line 28 to a heat exchanger 29, and
then returned to the bromination reactor.

1 [0035] Water from the flash vaporization unit (containing up to 3 wt% of molecular
bromine) is sent by a line 30 to a distillation unit 31, which yields water as the bottoms
stream and bromine or bromine-water azeotrope as a distillate. The distillate is returned
through a line 32 back to the flash vaporization unit.

5 [0036] The gaseous products of the flash vaporization unit (e.g., oxygen, nitrogen,
optionally other gases, and no more than a minor or trace amount of bromine) are carried by a
line 33 to a bromine scavenging unit 34, which separates molecular bromine from the other
gases. The recovered bromine is then carried by a line 35 through a heat exchanger 29 and
10 reintroduced into the bromination reactor. The amount of bromine entering the scavenger can
be further reduced by increasing the amount of bromine recovered in the flash step by
employing brine solutions and direct contact cooling to allow the use of temperatures below
0° Centigrade. The other gases (e.g., nitrogen, oxygen) can be vented to the atmosphere.

15 [0037] Various embodiments and features of individual subprocesses and other
improvements for carrying out the invention will now be described in more detail.

[0038] Bromination

20 [0039] Bromination of the hydrocarbon feedstock is carried out in a fixed bed, fluidized
bed, or other suitable reactor, at a temperature and pressure such that the bromination
products and reactants are gases, for example, 1-50 atm, 150-600 °C, more preferably 400-
600 °C, even more preferably, 450-515 °C, with a residence time of 1-60 seconds, more
preferably 1-15 seconds. Higher temperatures tend to favor coke formation, while low
temperatures require larger reactors. Using a fluidized bed offers the advantage of improved
25 heat transfer.

[0040] Alkane bromination can be initiated using heat or light, with thermal means being
preferred. In one embodiment, the reactor also contains a halogenation catalyst, such as a
zeolite, amorphous alumino-silicate, acidic zirconia, tungstates, solid phosphoric acids, metal
oxides, mixed metal oxides, metal halides, mixed metal halides (the metal in such cases
30 being, e.g., nickel, copper, cerium, cobalt, etc.), and/or or other catalysts as described, e.g., in
U.S. 3,935,289 and 4,971,664. In an alternate embodiment, the reactor contains a porous or
non-porous inert material that provides sufficient surface area to retain coke formed in the
reactor and prevent it from escaping. The inert material may also promote the formation of
polyhalogenated hydrocarbons, such as tribromopropane. In still another embodiment, both a
35 catalyst and an inert material are provided in the reactor. Optionally, the reactor contains
different regions or zones to allow, in or more zones, complete conversion of molecular
bromine to produce alkyl bromides and hydrogen bromide.

1 [0041] The bromination reaction can also be carried out in the presence of an
isomerization catalyst, such as a metal bromide (e.g., NaBr, KBr, CuBr, NiBr₂, MgBr₂,
CaBr₂), metal oxide (e.g., SiO₂, ZrO₂, Al₂O₃), or metal (Pt, Pd, Ru, Ir, Rh) to help generate
the desired brominated isomer(s). Since isomerization and bromination conditions are
5 similar, the bromination and isomerization can be carried out in the same reactor vessel.
Alternatively, a separate isomerization reactor can be utilized, located downstream of the
bromination reactor and upstream of the coupling reactor.

[0042] Reproportionation

10 [0043] In some embodiments, a key feature of the invention is the "reproportionation" of
polyhalogenated hydrocarbons (polyhalides), i.e., halogenated hydrocarbons containing two
or more halogen atoms per molecule. Monohalogenated alkanes (monohalides) created
during the halogenation reaction are desirable as predominant reactant species for subsequent
coupling reactions and formation of higher molecular weight hydrocarbons. For certain
15 product selectivities, polyhalogenated alkanes may be desirable. Reproportionation allows a
desired enrichment of monohalides to be achieved by reacting polyhalogenated alkyl halides
with nonhalogenated alkanes, generally in the substantial absence of molecular halogens, to
control the ratio of mono-to-polyhalogenated species. For example, dibromomethane is
reacted with methane to produce methyl bromide; dibromomethane is reacted with propane to
20 produce methyl bromide and propyl bromide and/or propylene; and so forth.

[0044] Reactive reproportionation is accomplished by allowing the hydrocarbon
feedstock and/or recycled alkanes to react with polyhalogenated species from the
halogenation reactor, preferably in the substantial absence of molecular halogen. As a
25 practical matter, substantially all of the molecular halogen entering the halogenation reactor
is quickly consumed, forming mono- and polyhalides; therefore reproportionation of higher
bromides can be accomplished simply by introducing polybromides into a mid- or
downstream region or "zone" of the halogenation reactor, optionally heated to a temperature
that differs from the temperature of the rest of the reactor.

30 [0045] Alternatively, reproportionation can be carried out in a separate "reproportionation
reactor," where polyhalides and unhalogenated alkanes are allowed to react, preferably in
the substantial absence of molecular halogen. FIG. 3 illustrates one such embodiment where,
for clarity, only significant system elements are shown. As in FIG. 1, natural gas or another
hydrocarbon feedstock and molecular bromine are carried by separate lines 1, 2 to a heated
35 bromination reactor 3 and allowed to react. Products (HBr, alkyl bromides) and possibly
unreacted hydrocarbons, exit the reactor and are carried by a line 4 into a first separation unit
5 (SEP I), where monobrominated hydrocarbons and HBr are separated from polybrominated

1 hydrocarbons. The monobromides, HBr, and possibly unreacted hydrocarbons are carried by
a line 7, through a heat exchanger 8, to a coupling reactor 9, and allowed to react, as shown in
FIG. 1. The polybromides are carried by a line 6 to a reproporationation reactor 36.

5 Additional natural gas or other alkane feedstock is also introduced into the reproporationation
reactor, via a line 37. Polybromides react with unbrominated alkanes in the reproporationation
reactor to form monobromides, which are carried by a line 38 to the coupling reactor 9, after
first passing through a heat exchanger.

[0046] In another embodiment of the invention (not shown), where the hydrocarbon
10 feedstock comprises natural gas containing a considerable amount of C2 and higher
hydrocarbons, the "fresh" natural gas feed is introduced directly into the reproporationation
reactor, and recycled methane (which passes through the reproporationation reactor
unconverted) is carried back into the halogenation reactor.

[0047] Reproporationation is thermally driven and/or facilitated by use of a catalyst.
15 Nonlimiting examples of suitable catalysts include metal oxides, metal halides, and zeolites.
U.S. 4,654,449 discloses the reproporationation of polyhalogenated alkanes with alkanes using
an acidic zeolite catalyst. U.S. 2,979,541 and 3,026,361 disclose the use of carbon
tetrachloride as a chlorinating agent for methane, ethane, propane and their chlorinated
analogues. All three patents are incorporated by reference herein in their entirety. Using
20 reproporationation in the context of a continuous process for the enrichment of reactive feed
stocks for the production of higher hydrocarbons has never been disclosed to our knowledge.

[0048] Reproporationation of C1-C5 alkanes with dibromomethane and/or other
polybromides occurs at temperatures ranging from 350 to 550 °C, with the optimal
25 temperature depending on the polybromide(s) that are present and the alkane(s) being
brominated. In addition, reproporationation proceeds more quickly at elevated pressures (e.g.,
2-30 bar). By achieving a high initial methane conversion in the halogenation reactor,
substantial amounts of di- and tribromomethane are created; those species can then be used as
bromination reagents in the reproporationation step. Using di- and tribromomethane allows
30 for controlled bromination of C1-C5 alkanes to monobrominated C1-C5 bromoalkanes and
C2-C5 olefins. Reproporationation of di- and tribromomethane facilitates high initial methane
conversion during bromination, which should reduce the methane recycle flow rate and
enrich the reactant gas stream with C2-C5 monobromoalkanes and olefins, which couple to
liquid products over a variety of catalysts, including zeolites. This is a major new process
35 advance.

[0049] In another embodiment of the invention, reproporationation is carried out without
first separating the polyhalides in a separation unit. This is facilitated by packing the

1 "reproportionation zone" with a catalyst, such as a zeolite, that allows the reaction to occur at
a reduced temperature. For example, although propane reacts with dibromomethane to form
bromomethane and bromopropane (an example of "reproportionation"), the reaction does not
5 occur to an appreciable degree at temperatures below about 500°C. The use of a zeolite may
allow reproportionation to occur at a reduced temperature, enabling species such as methane
and ethane to be brominated in one zone of the reactor, and di-, tri-, and other polybromides
to be reproportionated in another zone of the reactor.

[0050] Bromine Recovery During Decoking

10 [0051] Inevitably, coke formation will occur in the halogenation and reproportionation
processes. If catalysts are used in the reactor(s) or reactor zone(s), the catalysts may be
deactivated by the coke; therefore, periodic removal of the carbonaceous deposits is required.
In addition, we have discovered that, within the coke that is formed, bromine may also be
15 found, and it is highly desirable that this bromine be recovered in order to minimize loss of
bromine in the overall process, which is important for both economic and environmental
reasons.

[0052] Several forms of bromides are present: HBr, organic bromides such as methyl
bromide and dibromomethane, and molecular bromine. The invention provides means for
20 recovering this bromine from the decoking process. In a preferred embodiment, a given
reactor is switched off-line and air or oxygen is introduced to combust the carbon deposits
and produce HBr from the residual bromine residues. The effluent gas is added to the air (or
oxygen) reactant stream fed to the bromine generation reactor, thereby facilitating complete
bromine recovery. This process is repeated periodically.

25 [0053] While a given reactor is off-line, the overall process can, nevertheless, be operated
without interruption by using a reserve reactor, which is arranged in parallel with its
counterpart reactor. For example, twin bromination reactors and twin coupling reactors can
be utilized, with process gasses being diverted away from one, but not both, bromination
30 reactors (or coupling reactors) when a decoking operation is desired. The use of a fluidized
bed may reduce coke formation and facilitate the removal of heat and catalyst regeneration.

[0054] Another embodiment of the decoking process involves non-oxidative decoking
using an alkane or mixture of alkanes, which may reduce both the loss of adsorbed products
and the oxygen requirement of the process. In another embodiment of the decoking process,
35 an oxidant such as oxygen, air, or enriched air is co-fed into the bromination section to
convert the coke into carbon dioxide and/or carbon monoxide during the bromination
reaction, thus eliminating or reducing the off-line decoking requirement.

1 [0055] Alkyl halide Separation

5 [0056] The presence of large concentrations of polyhalogenated species in the feed to the coupling reactor can result in an increase in coke formation. In many applications, such as the production of aromatics and light olefins, it is desirable to feed only monohalides to the coupling reactor to improve the conversion to products. In one embodiment of the invention, a specific separation step is added between the halogenation/reproportionation reactor(s) and the coupling reactor.

10 [0057] For example, a distillation column and associated heat exchangers ("SEP I" in FIGS. 1 and 2) can be used to separate the monobromides from the polybrominated species by utilizing the large difference in boiling points of the compounds. The polybrominated species that are recovered as the bottoms stream can be reproportionated with alkanes to form monobromide species and olefins, either in the bromination reactor or in a separate reproportionation reactor. The distillation column can be operated at any pressure of from 1 to 50 bar. The higher pressures allow higher condenser temperatures to be used, thereby reducing the refrigeration requirement.

15 [0058] FIG. 4 illustrates one embodiment of a separation unit for separating monobromides from polybrominated species. Alkyl bromides from the bromination reactor are cooled by passing through a heat exchanger 50, and then provided to a distillation column 20 51 equipped with two heat exchangers 52 and 53. At the bottom of the column, heat exchanger 52 acts as a reboiler, while at the top of the column heat exchanger 53 acts as a partial condenser. This configuration allows a liquid "bottoms" enriched in polybromides (and containing no more than a minor amount of monobromides) to be withdrawn from the distillation column. The polybromides are passed through another heat exchanger 54 to 25 convert them back to a gas before they are returned to the bromination reactor (or sent to a separate reproportionation reactor) for reproportionation with unbrominated alkanes. At the top of the column, partial reflux of the liquid from the reflux drum is facilitated by the heat exchanger 53, yielding a vapor enriched in lighter components including methane and HBr, and a liquid stream comprised of monobromides and HBr (and containing no more than a 30 minor amount of polybromides).

35 [0059] Alternate distillation configurations include a side stream column with and without a side stream rectifier or stripper. If the feed from the bromination reactor contains water, the bottoms stream from the distillation column will also contain water, and a liquid-liquid phase split on the bottoms stream can be used to separate water from the polybrominated species. Due to the presence of HBr in the water stream, it can either be sent to a HBr absorption column or to the bromine generation reactor.

1 [0060] Catalytic coupling of alkyl halides to higher molecular weight products

15 [0061] The alkyl halides produced in the halogenation/reproportionation step are reacted over a catalyst to produce higher hydrocarbons and hydrogen halide. The reactant feed can also contain hydrogen halide and unhalogenated alkanes from the bromination reactor. According to the invention, any of a number of catalysts are used to facilitate the formation of higher hydrocarbon products from halogenated hydrocarbons. Nonlimiting examples include non-crystalline aluminosilicates (amorphous solid acids), tungsten/zirconia super acids, sulfated zirconia, aluminosilicates such as SAPO-34 and its framework-substituted analogues (substituted with, e.g., Ni or Mn), Zeolites, such as ZSM-5 and its ion-exchanged analogs, and framework substituted ZSM-5 (substituted with Ti, Fe, Ti + Fe, B, or Ga). Preferred catalysts for producing liquid-at-room-temperature hydrocarbons include ion-exchanged ZSM-5 having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio below 300, preferably below 100, and most preferably 30 or below. Nonlimiting examples of preferred exchanged ions include ions of Ag, Ba, Bi, Ca, Fe, Li, Mg, Sr, K, Na, Rb, Mn, Co, Ni, Cu, Ru, Pb, Pd, Pt, and Ce. These ions can be exchanged as pure salts or as mixtures of salts. The preparation of doped zeolites and their use as carbon-carbon coupling catalysts is described in Patent Publication No. US 2005/0171393 A1, at pages 4-5, which is incorporated by reference herein in its entirety.

20 [0062] In one embodiment of the invention a Mn-exchanged ZSM-5 zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30 is used as the coupling catalyst. Under certain process conditions, it can produce a tailored selectivity of liquid hydrocarbon products.

25 [0063] Coupling of haloalkanes preferably is carried out in a fixed bed, fluidized bed, or other suitable reactor, at a suitable temperature (e.g., 150-600 °C, preferably 275-425 °C) and pressure (e.g., 0.1 to 35 atm) and a residence time (τ) of from 1-45 seconds. In general, a relatively long residence time favors conversion of reactants to products, as well as product selectivity, while a short residence time means higher throughput and (possibly) improved economics. It is possible to direct product selectivity by changing the catalyst, altering the reaction temperature, and/or altering the residence time in the reactor. For example, at a moderate residence time of 10 seconds and a moderate temperature of 350 °C, xylene and mesitylenes are the predominant components of the aromatic fraction (benzene + toluene + xylenes + mesitylenes; "BTXM") produced when the product of a methane bromination reaction is fed into a coupling reactor packed with a metal-ion-impregnated ZSM-5 catalyst, where the impregnation metal is Ag, Ba, Bi, Ca, Co, Cu, Fe, La, Li, Mg, Mn, Ni, Pb, Pd, or Sr, and the ZSM-5 catalyst is Zeolyst CBV 58, 2314, 3024, 5524, or 8014, (available from Zeolyst International (Valley Forge, PA)). At a reaction temperature of 425 °C and a residence time of 40 seconds, toluene and benzene are the predominant products of the BTXM fraction. Product selectivity can also be varied by controlling the concentration of

1 dibromomethane produced or fed into the coupling reactor. Removal of reaction heat and
continuous decoking and catalyst regeneration using a fluidized bed reactor configuration for
the coupling reactor is anticipated in some facilities.

5 [0064] In one embodiment, the coupling reaction is carried out in a pair of coupling
reactors, arranged in parallel. This allows the overall process to be run continuously, without
interruption, even if one of the coupling reactors is taken off line for decoking or for some
other reason. Similar redundancies can be utilized in the bromination, product separation,
halogen generation, and other units used in the overall process.

10 [0065] Hydrocarbon product separation and halogen recovery

[0066] The coupling products include higher hydrocarbons and HBr. In the embodiments
shown in FIGS. 1 and 2, products that exit the coupling reactor are first cooled in a heat
exchanger and then sent to an absorption column. HBr is absorbed in water using a packed
15 column or other contacting device. Input water and the product stream can be contacted either
in a co-current or counter-current flow, with the counter-current flow preferred for its
improved efficiency. HBr absorption can be carried out either substantially adiabatically or
substantially isothermally. In one embodiment, the concentration of hydrobromic acid after
absorption ranges from 5 to 70wt%, with a preferred range of 20 to 50wt%. The operating
20 pressure is 1 to 50 bar, more preferably 1 to 30 bar. In the laboratory, a glass column or
glass-lined column with ceramic or glass packing can be used. In a pilot or commercial plant,
one or more durable, corrosion-resistant materials (described below) are utilized.

[0067] In one embodiment of the invention, the hydrocarbon products are recovered as a
25 liquid from the HBr absorption column. This liquid hydrocarbon stream is phase-separated
from the aqueous HBr stream using a liquid-liquid splitter and sent to the product cleanup
unit. In another embodiment, the hydrocarbon products are recovered from the HBr column
as a gas stream, together with the unconverted methane and other light gases. The products
are then separated and recovered from the methane and light gases using any of a number of
30 techniques. Nonlimiting examples include distillation, pressure swing adsorption, and
membrane separation technologies.

[0068] In some embodiments, the product clean-up unit comprises or includes a reactor
for converting halogenated hydrocarbons present in the product stream into unhalogenated
hydrocarbons. For example, under certain conditions, small amounts of C1-C4
35 bromoalkanes, bromobenzene, and/or other brominated species are formed and pass from the
coupling reactor to the liquid-liquid splitter 16 and then to the product clean-up unit 17.
These brominated species can be "hydrodehalogenated" in a suitable reactor. In one
embodiment, such a reactor comprises a continuous fixed bed, catalytic converter packed

1 with a supported metal or metal oxide catalyst, Nonlimiting examples of the active
component include copper, copper oxide, palladium, and platinum, with palladium being
preferred. Nonlimiting examples of support materials include active carbon, alumina, silica,
and zeolites, with alumina being preferred. The reactor is operated at a pressure of 0-150 psi,
5 preferably 0-5 psi, and a temperature of 250-400 °C, preferably 300-350 °C, with a GHSV of
1200-60 hr⁻¹, preferably ~240 hr⁻¹. When bromobenzene (e.g.) is passed over such a reactor,
it is readily converted to benzene and HBr, with some light hydrocarbons (e.g., C3-C7)
produced as byproducts. Although carbon deposition (coking) can deactivate the catalyst, the
catalyst can be regenerated by exposure to oxygen and then hydrogen at, e.g., 500 °C and 400
10 °C, respectively.

[0069] After HBr is separated from the hydrocarbon products, the unconverted methane
leaves with the light gases in the vapor outlet of the HBr absorption unit. In one embodiment
of the invention, unconverted methane is separated from the light gases in a separation unit
15 ("SEP II" in the FIGS.), which operates using pressure or temperature swing adsorption,
membrane-based separation, cryogenic distillation (preferable for large-scale production), or
some other suitable separation process. Low methane conversions in the bromination reactor
may result in the coupling products being carried with the light gases, which in turn would
necessitate the recovery of these species from the lights gases. Separation technologies that
20 can be employed for this purpose include, but are not limited to, distillation, pressure or
temperature swing adsorption, and membrane-based technologies.

[0070] In another aspect of the invention, a process for separating anhydrous HBr from
an aqueous solution of HBr is provided. HBr forms a high-boiling azeotrope with water;
therefore, separation of HBr from the aqueous solution requires either breaking the azeotrope
25 using an extractive agent or bypassing the azeotrope using pressure swing distillation. FIG. 5
illustrates one embodiment of an extractive distillation unit for separating HBr from water.
Water is extracted in a distillation column 200 and HBr is obtained as the distillate stream
201. The distillate stream may also contain small amounts of water. In one embodiment, the
distillation column 200 is a tray-tower or a packed column. Conventional ceramic packing is
30 preferred over structured packing. Aqueous bromide salt, such as CaBr₂, is added at the top
of the distillation column, resulting in the extraction of water from aqueous HBr. A
condenser may not be required for the column. A reboiler 203 is used to maintain the vapor
flow in the distillation column. The diluted stream of aqueous CaBr₂ 202 is sent to the
evaporation section 206, which, optionally has a trayed or packed section. The bottoms
35 stream from the column is heated before entering the evaporation section. Stream 207
comprising mostly water (and no more than traces of HBr) leaves the evaporation section.

1 [0071] In one embodiment, HBr is displaced as a gas from its aqueous solution in the
presence of an electrolyte that shares a common ion (Br^- or H^+) or an ion (e.g. Ca^{2+} or SO_4^{2-})
that has a higher hydration energy than HBr. The presence of the electrolyte pushes the
equilibrium $\text{HBr}_{\text{aq}} \leftrightarrow \text{HBr}_{\text{gas}}$ towards gas evolution, which is further facilitated by heating
5 the solution.

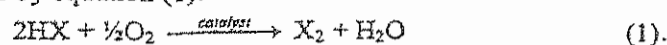
[0072] Aqueous solutions of metal bromides such as CaBr_2 , MgBr_2 also KBr , NaBr ,
 LiBr , RbBr , CsBr , SrBr_2 , BaBr_2 , MnBr_2 , FeBr_2 , FeBr_3 , CoBr_2 , NiBr_2 , CuBr_2 , ZnBr_2 , CdBr_2 ,
 AlBr_3 , LaBr_3 , YBr_3 , and BiBr_3 can be used as extractive agents, with aqueous solutions of
10 CaBr_2 , MgBr_2 , KBr , NaBr , LiBr or mixtures thereof being preferred. The bottoms stream of
the distillation column contains a diluted solution of the extracting agent. This stream is sent
to another distillation column or a vaporizer where water is evaporated and the extracting
agent is concentrated before sending it back to the extractive distillation column. Sulfuric
acid can be used as an extracting agent if its reaction with HBr to form bromine and sulfur
15 dioxide can be minimized. Experiments carried out to demonstrate the separation of
anhydrous HBr from an aqueous solution of HBr are described in Example 1 and 2.

[0073] In another aspect of the invention, various approaches to product clean-up
(separation and/or purification) are provided. A number of bromide species may be present
20 in the unpurified product stream: HBr, organic bromides such as methyl bromide and
dibromomethane, and bromo-aromatics. In one embodiment of the invention, hydrocarbon
products are separated from brominated species by passing the product stream over copper
metal, NiO , CaO , ZnO , MgO , BaO , or combinations thereof. Preferably, the products are run
over one or more of the above-listed materials at a temperature of from 25-600 °C, more
25 preferably, 400-500 °C. This process is tolerant of CO_2 that may be present.

[0074] In another embodiment, particularly for large-scale production of hydrocarbons,
unconverted methane is separated from other light hydrocarbons as well as heavier products
(e.g., benzene, toluene, etc.) using distillation. For example, in FIGS. 1 and 2, methane and
other light hydrocarbons exit the absorption column through a gas outlet and are directed to a
30 separation unit (SEP. II). Any unconverted methyl bromide will be removed with the light
gases and can be recycled back to the bromination/reproportionation reactor. Heavier
hydrocarbons are removed as a liquid distillate.

[0075] Molecular Halogen Generation

35 [0076] In one embodiment of the invention, catalytic halogen generation is carried out by
reacting hydrohalic acid and molecular oxygen over a suitable catalyst. The general reaction
can be represented by equation (1):

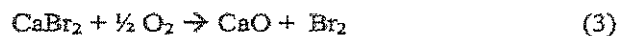
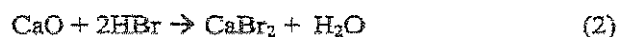


1 The process occurs at a range of temperatures and mole ratios of hydrohalic acid (HX) and
molecular oxygen (O₂), i.e., 4:1 to 0.001:1 HX/O₂, preferably 4:1 (to fit the reaction
stoichiometry), more preferably 3.5:1 (to prevent eventual HBr breakthrough).

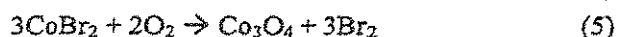
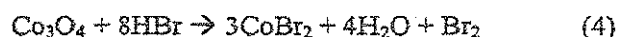
5 Halogen can be generated using pure oxygen, air, or oxygen-enriched gas, and the
reaction can be run with a variety of inert nonreacting gases such as nitrogen, carbon dioxide,
argon, helium, and water steam being present. Any proportion of these gases can be
combined as pure gases or selected mixtures thereof, to accommodate process requirements.

10 [0077] A number of materials have been identified as halogen generation catalysts. It is
possible to use one type of catalyst or a combination of any number, configuration, or
proportion of catalysts. Oxides, halides, and/or oxy-halides of one or more metals, such as
Cu, Ag, Au, Fe, Co, Ni, Mn, Ce, V, Nb, Mo, Pd, Ta, or W are representative, more preferably
Mg, Ca, Sr, Ba, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, or Ce. The most preferable catalysts are
oxides, halides, and/or oxy-halides of Cu.

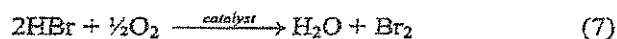
15 [0078] Although not bound by theory, the following equations are considered
representative of the chemistry believed to take place when such materials are used to
catalyze halogen formation:



for metal oxides in which the metal does not change oxidation states, and

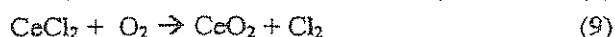
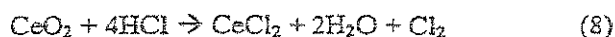


for metal oxides in which the metal does change oxidation states. The net reaction for (2)
+ (3) and (4) + (5) is (7):



which is equivalent to (1).

35 In one embodiment of the invention, chlorine is used as the halogenating agent, and
ceria (CeO₂) is used to catalyze the generation of chlorine from hydrochloric acid. The
following equations are considered representative:



1

for an overall reaction: $2\text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Cl}_2$ (10)

which is also equivalent to (1).

5 [0079] This use of ceria is quite novel, as it allows essentially complete consumption of HCl. In contrast, previous reactions of metal oxides, HCl, and oxygen have typically yielded HCl/Cl₂ mixtures. Thus, ceria can advantageously be employed as a halogen regeneration catalyst, particularly where chlorine is used for alkane halogenation, with chlorine's attendant lower cost and familiarity to industry.

10 [0080] In one embodiment of the invention, the halogen generation catalyst(s) are supported on porous or nonporous alumina, silica, zirconia, titania or mixtures thereof, or another suitable support. A range of temperatures can be employed to maximize process efficiency, e.g., 200-600 °C, more preferably 350-450 °C.

15 [0081] Recovery and recycle of molecular halogen

[0082] Halogen generation produces both water and molecular halogen. Water can be separated from halogen and removed before the halogen is reacted with the hydrocarbon feedstock. Where the halogen is bromine, a bromine-water, liquid-liquid phase split is achieved upon condensation of a mixture of these species. For example, in one embodiment 20 of the invention, a liquid-liquid flash unit is used to separate most of the bromine from water, simply and inexpensively. The bromine phase typically contains a very small amount of water, and can be sent directly to the bromination reactor. The water phase, however, contains 1-3 wt% bromine. However, if air is used in the bromine generation step, nitrogen and unconverted oxygen are present with the bromine and water stream that enters the flash.

25 [0083] The gas leaving the flash unit primarily consists of nitrogen and unconverted oxygen, but carries with it some bromine and water. The amount of bromine leaving with the vapor phase depends on the temperature and pressure of the flash. The flash can be operated at temperatures ranging from 0 to 50 °C; however, a lower temperature (ca 2 to 10 °C) is preferred to reduce bromine leaving in the vapor stream. The vapor stream is sent to the 30 bromine scavenging section for bromine recovery. In one embodiment, the operating pressure is 1 to 50 bar, more preferably 1 to 30 bar. Since water freezes at 0 °C, it is not possible to substantially reduce the temperature of the flash 19. However, the vapor stream from the flash can be contacted with a chilled brine solution, at temperatures from -30 °C to 35 10 °C. Chilled brine temperatures lower than that of the flash can substantially reduce the bromine scavenging requirement of the scavenging unit. Vaporizing the bromine by heating the brine can then occur, with further heating employed to facilitate concentration of the brine

1 for re-use. This approach to bromine recovery can be carried out either continuously or in batch mode.

5 [0084] Bromine contained in the water-rich phase leaving the liquid-liquid flash can be effectively recovered by distillation. Other means, such as using an inert gas to strip the bromine from the water phase (described by Waycuilis) and adsorption-based methods, are not very effective, and potentially can result in a significant loss of bromine. The presently described distillation subprocess produces bromine or bromine-water azeotrope as a distillate, which is recycled back to the flash unit. Water is contained in the bottoms stream. Bromine can react reversibly with water to form small amounts of HBr and HOBr. In the distillation scheme, therefore, ppm levels of HBr (and/or HOBr) can be present in the bottoms stream. A side-stream rectifier or stripper can be utilized to reduce the bromine content of the bottoms stream to produce a pure water stream. Other alternatives that can reduce the bromine content of the water to below 10 ppm range include, but are not limited to, the addition of acids such as sulfuric acid, hydrochloric acid, and phosphoric acid, in very small quantities to reduce the pH of the water stream. Lowering the pH drives the HBr and HOBr stream back to bromine and water, thereby substantially reducing the loss of bromine in the water stream. HBr present in the water stream can also be recovered using ion-exchange resins or electrochemical means.

20 [0085] Recovery of all halogen for reuse. For both economic and environmental reasons, it is preferred to minimize, if not completely eliminate, loss of halogen utilized in the overall process. Molecular bromine has the potential to leave with vented nitrogen and unconverted oxygen if it is not captured after Br₂ generation. Bromine scavenging can be carried out in a bed containing solid CuBr or MnBr₂, either loaded on a support or used in powder form, to capture Br₂ from a gas stream that may also contain H₂O, CO₂, O₂, methane &/or N₂. In one embodiment of the invention, bromine scavenging is performed within a range of temperatures, i.e., from -10 ° to 200 °C. When bromine scavenging is complete, molecular bromine can be released from the bed by raising the temperature of the bed to 220 °C or higher, preferably above 275 °C. It is important that there be little if any O₂ in the bed during bromine release, as O₂ will oxidize the metal and, over time, reduce the bromine-scavenging capacity of the bed.

30 [0086] Construction of critical process elements with unique corrosion-resistant materials

35 [0087] Corrosion induced by any halogen-containing process, whether in the condensed phase or the vapor phase, presents a significant challenge in the selection of durable materials for the construction of reactors, piping, and ancillary equipment. Ceramics, such as alumina, zirconia, and silicon carbides, offer exceptional corrosion resistance to most conditions encountered in the process described herein. However, ceramics suffer from a number of

1 disadvantages, including lack of structural strength under tensile strain, difficulty in
completely containing gas phase reactions (due to diffusion or mass transport along jointing
surfaces), and possibly undesirable thermal transport characteristics inherent to most ceramic
materials. Constructing durable, gas-tight, and corrosion resistant process control equipment
5 (i.e. shell and tube type heat-exchangers, valves, pumps, etc.), for operation at elevated
temperatures and pressures, and over extended periods of time, will likely require the use of
formable metals such as Au, Co, Cr, Fe, Nb, Ni, Pt, Ta, Ti, and/ or Zr, or alloys of these base
metals containing elements such as Al, B, C, Co, Cr, Cu, Fe, H, Ha, La, Mn, Mo, N, Nb, Ni,
O, P, Pd, S, Si, Sn, Ta, Ti, V, W, Y, and/or Zr.

10 [0088] According to one embodiment of the invention, the process and subprocesses
described herein are carried out in reactors, piping, and ancillary equipment that are both
strong enough and sufficiently corrosion-resistant to allow long-term continued operation.
Selection of appropriate materials of construction depends strongly on the temperature and
environment of exposure for each process control component.

15 [0089] Suitable materials for components exposed to cyclic conditions (e.g. oxidizing and
reducing), as compared to single conditions (oxidizing or reducing), will differ greatly.
Nonlimiting examples of materials identified as suitable for exposure to cyclic conditions,
operating in the temperature range of from 150-550 °C, include Au and alloys of Ti and Ni,
with the most suitable being Al/V alloyed Ti (more specifically Ti Grd-5) and Ni-Cr-Mo
20 alloys with high Cr, low Fe, and low C content (more specifically ALLCORR®, Alloy 59, C-
22, 625, and HX). Nonlimiting examples of materials identified as suitable for exposure to
either acid halide to air, or molecular halogen to air cyclic conditions, in the temperature
range 150-550 °C, either acid halide to air, or molecular halogen to air include alloys of Fe
and Ni, with the most suitable being alloys of the Ni-Cr-Mo, and Ni-Mo families.

25 Nonlimiting examples of materials identified as suitable for single environment conditions, in
the temperature range 100°C-550°C, include Ta, Au, and alloys of Fe, Co, and Ni. For lower
temperature conditions (<280°C), suitable polymer linings can be utilized such as PTFE,
FEP, and more suitably PVDF. All materials may be used independently or in conjunction
with a support material such as coating, cladding, or chemical/physical deposition on a
30 suitable low-cost material such as low-alloy steels.

[0090] Figure 6 schematically illustrates an alternate mode of operation for a continuous
process for converting methane, natural gas, or other alkane feedstocks into higher
hydrocarbons. Alkanes are brominated in the bromination section in the presence of water
35 formed during bromine generation, including recycled water. The bromination products pass
either through a reproporationation reactor or through the reproporationation section of the
bromination reactor, where the light gases are reproporationated to form olefins and alkyl
bromides by using the polybromides as brominating agents. The reproporationation products,

1 which include olefins, alkyl monobromides, some polybromides, and HBr, along with any
unreacted alkanes, are then sent to the coupling reactor. The coupling products are sent to a
vapor-liquid-liquid flash. Higher hydrocarbon products are removed as an organic phase
from the vapor-liquid-liquid flash, while aqueous HBr is removed as the heavier phase. The
5 gas stream from the flash is sent to a separation system to recover methane and light gases,
which are recycled back to the bromination and reproporationation sections, respectively.

[0091] Nitrogen must be removed from the gas recycle stream if air is used as an oxidant
in bromine generation. The aqueous HBr stream coming out of the vapor-liquid-liquid flash
10 is sent to the HBr/water separation system, where water is recovered. The separation can be
carried out in a distillation column, where pure water is taken out as a distillate and the
bottoms stream is an aqueous solution of HBr (having a higher concentration of HBr than the
feed to the distillation column). The aqueous HBr stream is sent back to the bromine
generation section, where bromine is generated from aqueous HBr in the presence of air or
15 oxygen.

[0092] Alternatively, extractive distillation is used to separate HBr from water. The
separated HBr is sent to the bromine generation reactor and bromine is generated from
aqueous HBr in the presence of air or oxygen. Complete conversion of HBr is not necessary
20 in the bromine generation reactor. Periodic decoking can be carried out for the bromination,
reproporationation, and/or coupling reactors, with the bromine-containing decoking product
stream being routed to the bromine generation reactor.

[0093] Another continuous process alternative is shown in FIG. 7. Alkanes are
brominated in the bromination section in the presence of water formed during bromine
25 generation, including recycled water. The bromination products (which include
monobromides and polybromides) pass through either a reproporationation reactor or the
reproporationation section of the bromination reactor, where the light gases are
reproporationated to form alkyl bromides, using the polybromides as brominating agents. The
reproporationation products -- alkyl monobromides, olefins, a small amount of polybromides,
30 and HBr -- and any unreacted alkanes are then sent to a separation unit where aqueous HBr is
separated from the alkyl bromides. Monobromides in the alkyl bromide stream are separated
from the polybromides. The polybromides are recycled to the reproporationation section
where polybromides react with the recycle gases to form olefins and monobromides.

35 [0094] The aqueous HBr separation from the alkyl bromides can be carried out in a
distillation column coupled with a liquid-liquid flash. The alkyl bromide stream can contain
HBr. The monobromides are fed into the coupling section, and the products are sent to a
water absorption column where HBr produced in the coupling reactor is removed from the

1 products and unconverted gas. The liquid outlet of the absorption column is fed to a vapor-
liquid-liquid flash separation unit, where higher hydrocarbon products are removed as an
organic phase and aqueous HBr is removed as the heavier phase. The gas outlet from the
absorption column is sent to a separation system to separate methane from the light gases.
5 The recovered methane is recycled back to the bromination section, while the light gases are
recycled to the reproporationation section.

[0095] Nitrogen must be separated before the gases are recycled if air is used as an
oxidant in bromine generation. The aqueous HBr stream from the vapor-liquid-liquid flash is
10 combined with the aqueous HBr stream from the alkyl bromide separation section and sent to
the HBr/Water separation system. The separation can be carried out in a distillation column,
where pure water is taken out as a distillate and the bottoms stream is an aqueous solution of
HBr having a higher concentration of HBr compared with the feed to the distillation column.
The aqueous HBr stream is sent back to the bromine generation section, where bromine is
15 generated from aqueous HBr in the presence of air, oxygen or enriched air.

[0096] Alternatively, extractive distillation is used to separate HBr from water. The
separated HBr is sent to the bromine generation reactor, where bromine is generated from
aqueous HBr in the presence of air, oxygen, or enriched air. Complete conversion of HBr to
bromine is not required during bromine generation. Periodic decoking of the bromination,
20 reproporationation and coupling reactors can be carried out, with the bromine-containing
decoking product stream being routed to the bromine generation reactor.

[0097] The following are nonlimiting examples of the invention and various subprocesses
for practicing the invention.

[0098] Example 1. Reproporationation of Dibromomethane with Propane

[0099] Methane (11 sccm, 1 atm) was combined with nitrogen (15 sccm, 1 atm) at room
temperature via a mixing tee and passed through a room temperature bubbler full of bromine.
The CH₄/N₂/Br₂ mixture was plumbed into a preheated glass tube at 500 °C, and bromination
of the methane took place with a residence time ("t_{res}") of 60 seconds, producing primarily
bromomethane, dibromomethane, and HBr. The stream of nitrogen, HBr, and partially
30 brominated hydrocarbon was combined with propane (0.75 sccm, 1 atm) in a mixing tee and
passed into a second glass reactor tube at 525 °C with a residence time ("t_{res}") of 60 s. In the
second reactor tube, polybrominated hydrocarbons (i.e. CH₂Br₂, CHBr₃) react with the
propane to produce bromopropanes. The reproporationation is idealized by the following
reaction:



As products left the second reactor, they were collected by a series of traps containing 4 M
NaOH (which neutralized the HBr) and hexadecane (containing octadecane as an internal
standard) to dissolve as much of the hydrocarbon products as possible. Volatile components

like methane and propane were collected in a gas bag after the HBr/hydrocarbon traps. All products were quantified by gas chromatography. The results ("Ex. 1") are summarized in Table 1. For comparison, the reactions were also run with two reactors, but without reproporationation with propane ("Control A"), and with only the first reactor and without propane ("Control B").

Table 1. Reproporationation of Dibromomethane

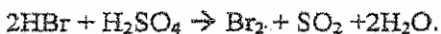
	Ex. 1 (bromination/ reproporationation)	Control A (bromination)	Control B (bromination)
Bromination t_{res}	60	60	60
Reproporationation t_{res}	60	60	0
CH ₄ conversion	40%	47%	45%
CH ₃ Br/(CH ₃ Br+CH ₂ Br ₂)	93%	84%	74%
C ₃ H ₈ conversion	85%	N/A	N/A
Carbon balance	96%	97%	96%

[00100] Example 2. Separation of Anhydrous HBr

[00101] 20 ml stock HBr aqueous solution were added to 20 g CaBr₂·H₂O followed by heating to 70 °C. A significant evolution of HBr gas was observed (determined by AgNO₃ precipitation and the NH₃ fuming test). The released HBr was not quantified as the reaction was carried out in an open vessel.

[00102] Example 3. Separation of Anhydrous HBr

[00103] Dehydration with H₂SO₄ was attempted by adding a conc. solution of H₂SO₄ to HBr. Qualitative tests were conducted in which different concentration of H₂SO₄ were added to HBr for determination of the threshold concentration where oxidation of HBr no longer occurs:



[00104] It was determined that the H₂SO₄ concentration below which no oxidation is apparent is ~ 70 wt.%. 30 ml 70 % H₂SO₄ was added to 30 ml stock HBr azeotrope (48 wt.%) and the mixture was heated to boiling. The HBr content was determined quantitatively by AgNO₃ precipitation and gravimetric determination of AgBr from a solution aliquot at the moment of mixing, after 15 min and after 30 min. boiling.

[00105] Example 4. Metathesis of Brominated Methane over Selected Catalysts

1 [00106] A series of experiments were conducted in which methane was brominated in a
 manner substantially the same as or similar to that described in Example 1 (10 sccm methane
 bubbled through room temperature bromine, followed by passage of the mixture through a
 reactor tube heated to 500°C), and the bromination products were then passed over various
 5 metal-ion exchanged or impregnated zeolite catalysts, at atmospheric pressure (total
 pressure), at a temperature of from 350 to 450 °C, with a residence time of 40 seconds. Table
 2 summarizes the distribution of metathesis products. Catalysts are denoted by metal ion
 (e.g., Ba, Co, Mn, etc.) and by type of Zeolyst Int'l. zeolite (e.g., 5524, 58, 8014, etc.). The
 mass (mg) of each product, as well as the total mass of products is given for each run. The
 10 abbreviations, B, PhBr, T, X, and M refer to benzene, phenyl bromide, toluene, xylene, and
 mesitylene, respectively.

[00107] Table 2. Metathesis of Brominated Methane Over Selected Catalysts.

	T (C)	Catalyst	B	PhBr	T	X	M	Total (mg)
15	350	Ba 5524	0.25	0.00	0.96	2.58	3.14	6.93
	350	Ba 58	0.31	0.00	1.48	3.20	3.11	8.11
	350	Ba 8014	0.30	0.00	1.30	2.87	3.15	7.60
	350	Ca 58	0.20	0.00	0.81	2.44	3.09	6.53
20	350	Co 2314	1.22	0.02	3.05	2.18	0.56	7.04
	350	Co 3024	0.36	0.00	2.06	4.21	3.47	10.10
	350	Co 58	0.20	0.00	1.05	2.91	3.34	7.50
	350	Mg 3024	0.31	0.00	1.53	3.59	3.89	9.32
	350	Mg 58	0.28	0.00	1.41	3.30	3.43	8.42
25	350	Mn 2314	1.07	0.03	2.86	2.26	0.65	6.86
	350	Mn 3024	0.53	0.00	2.92	4.80	3.02	11.27
	350	Mn 58	0.17	0.00	0.88	2.70	3.62	7.37
	350	Ni 2314	1.12	0.05	2.94	2.44	0.74	7.29
	350	Ni 3024	0.61	0.00	2.82	3.85	2.13	9.41
30	375	Ba 5524	0.32	0.00	1.32	2.82	2.57	7.04
	375	Ba 58	0.40	0.00	1.84	2.93	2.40	7.57
	375	Ba 8014	0.32	0.00	1.23	2.84	2.95	7.34
	375	Ca 58	0.20	0.00	0.96	2.55	2.93	6.64
	375	Co 3024	0.47	0.00	2.30	3.52	2.18	8.48
35	375	Co 58	0.30	0.00	1.54	2.83	2.42	7.10
	375	Mg 3024	0.37	0.00	1.81	3.26	2.78	8.22
	375	Mg 58	0.34	0.00	1.67	3.04	2.74	7.80
	375	Mn 3024	0.62	0.00	2.91	3.90	2.17	9.59

1	375	Mn 58	0.22	0.00	1.18	2.71	2.83	6.94
	375	Pd 2314	1.54	0.00	3.10	1.83	0.37	6.85
	400	Ba 5524	0.46	0.00	2.37	4.16	2.95	9.94
	400	Ba 58	0.70	0.00	3.15	3.91	2.70	10.47
5	400	Ba 8014	0.38	0.00	1.57	3.81	3.77	9.53
	400	Ca 58	0.41	0.00	1.89	3.43	2.81	8.54
	400	Co 3024	0.78	0.00	3.42	4.14	2.26	10.60
	400	Co 58	0.62	0.00	2.71	3.36	2.31	8.99
10	400	Mg 3024	0.76	0.00	3.26	4.11	2.64	10.76
	400	Mg 58	0.71	0.00	3.04	3.74	2.59	10.08
	400	Mn 3024	0.98	0.00	4.10	4.38	2.06	11.52
	400	Mn 58	0.48	0.00	2.26	3.44	2.64	8.82
15	400	Ni 3024	0.81	0.00	3.15	3.35	1.72	9.04
	400	Pb 2314	1.20	0.03	3.25	3.27	1.20	8.94
	400	Pb 3024	1.07	0.04	2.77	3.63	1.66	9.17
	400	Pd 2314	2.44	0.00	3.16	1.22	0.18	7.01
20	400	Sr 2314	2.13	0.01	4.05	2.29	0.46	8.94
	400	Sr 3024	1.93	0.05	4.03	2.67	0.65	9.32
	425	Ag 3024	2.79	0.02	4.16	1.78	0.29	9.04
	425	Ag 8014	3.09	0.02	3.52	1.09	0.16	7.88
25	425	Ba 5524	0.54	0.00	2.67	3.67	2.33	9.22
	425	Ba 58	0.79	0.00	3.00	2.94	1.75	8.48
	425	Bi 2314	3.13	0.03	4.47	1.61	0.23	9.48
	425	Co 2314	3.39	0.03	4.34	1.59	0.25	9.60
30	425	Co 3024	1.07	0.00	3.42	2.79	1.09	8.38
	425	Cu 2314	2.89	0.02	4.74	2.13	0.37	10.15
	425	Li 5524	1.51	0.04	3.31	3.27	1.12	9.24
	425	Mg 3024	0.99	0.00	3.28	2.85	1.37	8.48
35	425	Mg 58	0.81	0.00	2.62	2.16	1.11	6.70
	425	Mn 3024	1.22	0.00	3.90	3.01	1.14	9.27
	425	Mo 2314	3.06	0.04	4.02	1.46	0.24	8.82
	425	Ni 3024	0.97	0.00	3.38	2.85	1.32	8.51
40	425	Sr 3024	2.53	0.02	4.36	2.22	0.43	9.56
	450	Ag 3024	3.84	0.02	4.27	1.36	0.18	9.67
	450	Bi 2314	3.90	0.01	3.59	0.67	0.06	8.23
	450	Ca 2314	3.64	0.02	4.10	1.00	0.16	8.92
45	450	Co 2314	4.12	0.01	3.77	0.77	0.08	8.75
	450	Cu 2314	3.65	0.00	4.30	1.10	0.14	9.19

1	450	Fe 2314	4.42	0.02	3.43	0.74	0.09	8.69
	450	Fe 3024	3.61	0.01	2.96	0.63	0.08	7.28
	450	Fe 5524	3.99	0.03	3.63	0.85	0.11	8.60
	450	La 2314	3.48	0.01	3.81	0.87	0.12	8.29
5	450	Li 8014	1.74	0.02	2.61	2.67	0.84	7.89
	450	Mg 2314	4.20	0.02	3.84	0.76	0.10	8.92
	450	Mn 2314	3.78	0.02	3.90	0.88	0.12	8.70
	450	Mo 2314	3.88	0.01	3.26	0.58	0.06	7.79
	450	Ni 2314	4.39	0.01	3.12	0.44	0.03	8.00
10	450	Pb 2314	2.58	0.01	4.68	2.31	0.45	10.02
	450	Pb 3024	2.08	0.01	4.44	2.87	0.70	10.10
	450	Pb 5524	1.89	0.02	3.58	2.71	0.73	8.93
	450	Pd 2314	4.03	0.00	1.58	0.14	0.00	5.76
	450	Sr 2314	3.71	0.00	4.78	1.68	0.21	10.39
15	450	Sr 3024	2.51	0.01	3.76	1.61	0.26	8.14

[00108] Example 5. Hydrodehalogenation of Bromobenzene, and Catalyst Regeneration

[00109] A test solution (1.5ml/hr), which includes 1.9wt% bromobenzene (PhBr) dissolved in dodecane, diluted by N₂ (1.1ml/min) was fed into a tubular quartz reactor in which 3.6g of highly dispersed precious metal catalyst (Pd/Al₂O₃, 0.5wt %) was loaded. The reaction was carried out at 325 °C with a residence time of 15s. The reaction effluent was trapped in a bubbler with 8ml 4M NaOH solution pre-added. The carrier gas as well as the gaseous product were collected in a gas bag. All of the carbon-based products in the gas phase and oil phase in the liquid product were subjected to GC analysis. For the base trap solution, the HBr concentration was measured with an ion-selective electrode. Based on all of these measurements, carbon and bromine balances were calculated.

[00110] The experiment was continuously run for over 300 hours until the conversion of PhBr dropped from 100% in the initial 70 hrs to below 30% (Fig. 8). Hydrodebromination of PhBr took place over the catalyst bed with the formation of benzene ("BZ") and HBr as the major products, accompanied with some light hydrocarbons (C₃-C₇) being detected as byproducts, which originated from solvent decomposition. Carbon deposition was recognized as the primary reason for deactivation of the catalyst. The catalyst proved to be re-generable via decoking at 500 °C with O₂ oxidation (5ml/min) for 10 hrs, followed by H₂ reduction (20ml/min) at 400 °C for 3hrs. The regenerated catalyst was identified to be as effective as the fresh catalyst, as confirmed by its ability to catalyze the same hydrodebromination reaction without activity loss in the first 70 hours (Fig. 9).

1 [00111] The invention has been described with references to various examples and
preferred embodiments, but is not limited thereto. Other modifications and equivalent
arrangements, apparent to a skilled person upon consideration of this disclosure, are also
5 included within the scope of the invention. For example, in an alternate embodiment of the
invention, the products 25 from the bromine generation reactor are fed directly into the
bromination reactor 3. The advantage of such a configuration is in eliminating the bromine
holdup needed in the flash unit 27, thereby reducing the handling of liquid bromine. Also, by
eliminating the bromine scavenging section including units 26, 27, 31 and 34, the capital cost
10 for the process can be reduced significantly. For energy efficiency, it is desirable to have the
outlet of bromine generation be equal to the bromination temperature. For bromine
generation, cerium-based catalysts are therefore preferred over copper-based catalysts in this
embodiment, since cerium bromide has a higher melting point (722 °C) than copper (I)
bromide (504 °C). The presence of oxygen in bromination and coupling reduces the
15 selectivity to the desired products; therefore, the bromine generation reactor must consume
all of the oxygen in the feed. In this embodiment, the monobromide separation 5 must be
modified to remove water using a liquid-liquid split on the bottoms stream of the distillation
column 51. The water removed in the liquid-liquid split contains HBr, which can be removed
from water using extractive distillation (see, e.g., FIG. 5), and then recycled back to the
bromine generation section.

20 [00112] Still other modifications are within the scope of the invention, which is limited
only by the accompanying claims and their equivalents.

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What is claimed is:

1. A method comprising:

providing a halogen stream;

providing a first alkane stream;

reacting at least a portion of the halogen stream with at least a portion of the first alkane stream to form a halogenated stream, wherein the halogenated stream comprises alkyl monohalides, alkyl polyhalides, and a hydrogen halide;

providing a second alkane stream;

reacting at least a portion of the second alkane stream with at least a portion of the alkyl polyhalides to create at least some additional alkyl monohalides; and

contacting at least some of the alkyl monohalides and at least some of the additional alkyl monohalides with a catalyst to form a product stream that comprises higher hydrocarbons and hydrogen halide.

2. The method of claim 1 further comprising:

separating the hydrogen halide from the product stream; and

reacting the hydrogen halide with a source of oxygen to regenerate the halogen stream.

3. The method of claim 2, wherein hydrogen halide is reacted with the source of oxygen in the presence of a cerium oxide catalyst.

4. The method of claim 1 wherein the reacting at least a portion of a halogen stream with at least a portion of the first alkane stream occurs in a first zone of a reactor vessel and the reacting at least a portion of the second alkane stream with at least a portion of the alkyl polyhalides occurs in a second zone of the reactor vessel.

5. The method of claim 4 wherein the first zone of the reactor vessel is upstream of the second zone of the reactor vessel.

6. The method of claim 1 where the reacting at least a portion of the halogen stream with at least a portion of the first alkane stream occurs in the presence of a halogenation catalyst.

7. The method of claim 6 wherein the halogenation catalyst comprises at least one catalyst selected from the group consisting of: a zeolite, an amorphous alumino-silicate, an acidic zirconia, a tungstate, a solid phosphoric acid, a metal oxide, a mixed metal oxide, a metal halide, and a mixed metal halide.

8. The method of claim 2 wherein the reacting at least a portion of the halogen stream with at least a portion of the first alkane stream occurs in a plurality of reactors, wherein at least one of the plurality of reactors is operating at all times.

9. The method of claim 8 wherein one of the plurality of reactors undergoes decoking by introduction of an oxygen source to produce a decoking product, wherein the decoking product is combined with the hydrogen halide before reacting the hydrogen halide with a source of oxygen.

10. The method of claim 1 further comprising:

contacting the at least some of the alkyl monohalides and at least some of the additional alkyl monohalides with an isomerization catalyst to create an isomerized stream prior to contacting the isomerized stream with the catalyst to form the product stream.

11. The method of claim 1 further comprising:

contacting the product stream with a hydrodehalogenation catalyst to create a dehalogenated product stream and hydrogen halide.

12. The method of claim 11 wherein the hydrodehalogenation catalyst comprises at least one active component selected from the group consisting of: copper, copper oxide, palladium, and platinum, and supported on at least one material selected from the group consisting of: an active carbon, an alumina, a silica, and a zeolite.

13. The method of claim 1 wherein the catalyst comprises an ion exchanged zeolite, wherein the ion comprises at least one ion selected from the group consisting of: a Ag ion, a Ba ion, a Bi ion, a Ca ion, an Fe ion, a Li ion, a Mg ion, a Sr ion, a K ion, a Na ion, a Rb ion, a Mn ion, a Co ion, a Ni ion, a Cu ion, a Ru ion, a Pb ion, a Pd ion, a Pt ion, and a Ce ion.

14. A system for forming hydrocarbons comprising:

a halogenation reactor, wherein the halogenation reactor receives a quantity of halide and a first quantity of alkane and produces a halogenated product, the halogenated product comprising an alkyl monohalide product and an alkyl polyhalide product;

a reproporationation reactor, wherein the reproporationation reactor receives the halogenated product and a second quantity of alkane and produces at least some additional alkyl monohalide product and a quantity of hydrogen halide; and

an oligomerization reactor comprising a catalyst, wherein the oligomerization reactor receives the alkyl monohalide product and the additional alkyl monohalide product and produces a quantity of hydrocarbon product and a second quantity of hydrogen halide.

15. The system of claim 14 further comprising:

a separator, wherein the separator receives the quantity of hydrocarbon product, the quantity of hydrogen halide, and the second quantity of hydrogen halide and produces an acid stream comprising substantially all of the hydrogen halide and a gas stream containing substantially all of the hydrocarbon product; and

an oxidation reactor, wherein the oxidation reactor receives the acid stream and a quantity of oxygen source material and produces at least a quantity of halogen.

16. The system of claim 14 wherein the halogenation reactor is located in a first zone of a reactor vessel and the reproporationation reactor is located in a second zone of the reactor vessel.

17. The system of claim 16 wherein the first zone is located upstream of the second zone.

18. The system of claim 15 further comprising:

a dehydrohalogenation reactor comprising a dehydrohalogenation catalyst, wherein the dehydrohalogenation reactor receives the gas stream containing substantially all of the hydrocarbon product and produces a dehalogenated gas stream and a third quantity of hydrogen halide.

19. The system of claim 14 further comprising:

an isomerization reactor comprising an isomerization catalyst, wherein the isomerization reactor receives the additional alkyl monohalide product and produces an isomerized alkyl monohalide that is transported to the oligomerization reactor.

20. The system of claim 14 wherein the halogenation reactor contains a catalyst.

21. The system of claim 20 wherein the halogenation catalyst comprises at least one catalyst selected from the group consisting of: a zeolite, an amorphous alumino-silicate, an acidic zirconia, a tungstate, a solid phosphoric acid, a metal oxide, a mixed metal oxide, a metal halide, and a mixed metal halide.

22. The system of claim 14 wherein the oligomerization reactor is operated at a temperature of between about 150 °C to about 600 °C.

23. The system of claim 14 wherein at least one of the halogenation reactor, the reproporationation reactor, and the oligomerization reactor comprises at least one material of construction selected from the group consisting of: Au, Co, Cr, Fe, Nb, Ni, Pt, Ta, Ti, Zr, and alloys of these base metals.

24. The system of claim 14 wherein at least one of the halogenation reactor, the reproporationation reactor, and the oligomerization reactor comprises a fixed bed reactor or a fluidized bed reactor.

25. A method comprising:

providing an alkyl halide stream comprising alkyl monohalides, alkyl polyhalides, and a hydrogen halide;

providing a first alkane stream;

reacting at least a portion of the first alkane stream with at least a portion of the alkyl halide stream to create at least some additional alkyl monohalides;

contacting at least some of the alkyl monohalides and at least some of the additional alkyl monohalides with a catalyst to form a product stream that comprises higher hydrocarbons, hydrogen halide, and any unreacted portion of the first alkane stream;

separating the unreacted portion of the first alkane stream from the product stream;

providing a halogen stream; and

reacting at least some of the unreacted portion of the first alkane stream separated from the product stream with the halogen to form the alkyl halide stream.